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THE CAUSE OF EXPLOSIONS IN OLD MK 102 MOD 0 BATTERIES UNDER DIS--ETC(U)
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NSWC TECHNICAL REPORT

WHITE OAK LABORATORY

THE CAUSE OF EXPLOSIONS IN OLD MK 102 MOD 0 BATTERIES UNDER DISCHARGE

BY
L.E. DeVries

12 APRIL 1977

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Two Mk 102 Mod 0 batteries exploded during discharge. An investigation indicated that the batteries had dead cells prior to discharge. The cells in the battery are alkaline zinc-mercuric oxide cells. Discharging this type of battery containing a dead cell can cause the cell to explode. It is recommended that the battery not be discharged when the open circuit voltage reaches 39.2v or below (indicating a dead cell).

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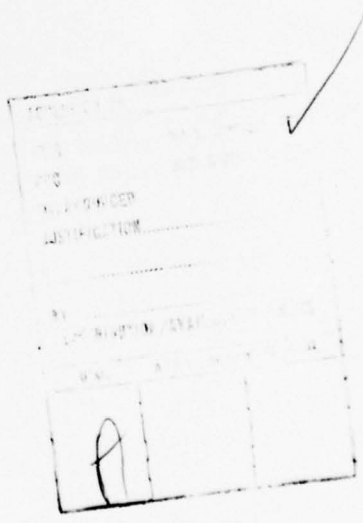
THE CAUSE OF EXPLOSIONS IN OLD MK 102 MOD 0 BATTERIES UNDER DISCHARGE

The discharge capacity of batteries decreases with time. Periodic replacement of old batteries is necessary to insure that the system containing them will operate. To avoid replacing batteries too early, the discharge capacity of old batteries needs to be determined. Two old Mk 102 Mod 0 batteries exploded while being discharged. The cause of the explosion and the method of preventing it are given in this report. This work was done under AN/BST 1 Engineering Support Task No. 9003.

J. R. DIXON
By direction



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INTRODUCTION

The Mk 102 Mod 0 battery is used for the electrical power in an emergency submarine location beacon. The alkaline zinc-mercuric oxide battery is manufactured by the Mallory Battery Company. As the battery ages, it reaches a point where it will no longer meet the power requirements of the beacon and is replaced by a new battery. A program was established at the Naval Surface Weapons Center, White Oak Laboratory (NSWC/WOL) to measure the capacity of the batteries that were being replaced. The old Mk 102 Mod 0 batteries were discharged under conditions simulating those in the beacon. Two batteries exploded during discharge. In each battery a single cell had exploded. One battery had a hole blown in the 7.9 mm thick base of the aluminum case, Figure 1. The other battery had the 10.3 mm thick aluminum lid bent upwards shearing some of 1/4-20 UNC steel screws that held it to the case, Figure 2. The conclusion reached on the cause of the explosions and the reasons for reaching it are given in the following material. Also given is the method for preventing explosions in the future.

BATTERY VOLTAGE AND DISCHARGE PROGRAM

Each battery contains 30 cells in three 10-cell sections. The cell is described in reference 1. Each cell has an open circuit voltage (OCV) of 1.35 V. The cells are series connected to give a nominal battery voltage of 40.5 V. Under the discharge program the battery is on a 4200 s (70 min) cycle. It is pulsed for 345 s (5.75 min) and then remains on a 0.1 A load the remaining 3855 s (64.25 min). During pulsing the load is repetitively changed from 0.1 to 5 A. The total times are 216.36 s (3.606 min) per cycle at 5 A and 3983.64 s (66.394 min) per cycle at 0.1 A. The battery is discharged at 271 K (28^{o}F) to a test voltage of 20.0 V.

NECESSARY CONDITIONS FOR THE EXPLOSION

It was under the above discharge conditions that the batteries, serial number (SN) 210 and SN 705, exploded. We believe that an explosion can only occur during discharge of a battery that contains at least one dead cell (a cell with 0 OCV). During discharge live cells cause dead cells to generate enough gas by electrolysis of the water in the alkaline electrolyte, (1), to cause the battery

$$H_2O \rightarrow 1/2\ O_2 + H_2 \qquad (1)$$

1. F. Fagan, Y. L. Ko, and R. E. Ralston. Proc. Power Sources Conf., 25, 21 (1972).

to explode. Table 1 gives the experimental data for SN 210 and SN 705. The calculated maximum pressure that could have been created in the dead cells, based on reaction (1), is also given.

INVESTIGATION AND OBSERVATIONS

Three batteries not discharged were examined to determine the state of their cells prior to discharge. The data for them is given in Table 2. Chemical analysis revealed that there was no unoxidized zinc in the dead cells. The live cells contained between 50 and 60% unoxidized zinc. In the live cells the loss of zinc was caused by corrosion of the zinc anode, (2). The alkaline electrolyte

$$Zn + H_2O \rightarrow ZnO + H_2 \qquad (2)$$

facilitated this reaction. Corrosion was expected in all cells, but the amount of zinc corroded had not been determined previously. The live cells contained only a small amount of liquid mercury as can be seen in Figure 3. The mercury was in the cathode. The dead cells contained a lot more liquid mercury, Figure 4. The mercury was distributed throughout the dead cells even in the zinc oxide in the anode. The large quantity of mercury in the dead cells was formed by discharge, (3). This indicates that an internal short

$$Zn + HgO \rightarrow ZnO + Hg \qquad (3)$$

circuit in each dead cell caused the uncorroded zinc to be oxidized.

POSSIBLE MECHANISMS FOR THE EXPLOSION

The question raised is why do batteries not explode because of the gas pressure built up by the corrosion of zinc, (2)? Even though batteries SN 750 and SN 751 would have had enough gas generated by corrosion to equal 61 MPa (8.8 kpsi), they did not explode. Seventy-one batteries constructed in the same manner have been received at NSWC/WOL. None have exploded because of the gas pressure produced by the corrosion reaction. The reason they do not explode is that the hydrogen is formed slowly over a long period of time, 4 years for SN 750 and SN 751. It diffuses out of the battery before a dangerous pressure has built up.

A high pressure rupture is a possible mechanism for an explosion. Each cell is sealed by crimping the wall of the cell into a rubber insulating ring on the lid. It is doubtful that such a seal can hold gas at a much higher pressure than 0.7 MPa (100 psi) without venting. Both live and dead cells from three batteries (SN 750, SN 751, and SN 793) were examined. The cells had been stripped of their coating about a week before being opened. When they were vented prior to being opened, the gas pressure was only about 0.07 MPa (10 psi). However, the cells are not bare in the battery. Ten cells are strapped together to form a cell stack. Each stack

is coated with an elastomer and placed in the aluminum battery case. The case is then filled with an epoxy resin. Filled sections are visible in Figure 2. This type of construction can permit the slow diffusion of hydrogen out of the battery as mentioned in the last paragraph. However, this type of construction might contain enough gas when it is generated in about 100 hours of discharge to create a high pressure. When the pressure exceeds what the structure can support, an explosion occurs. In the two batteries that exploded, the gas was being generated in a time period 250 (SN 210) to 630 (SN 705) times shorter than it was formed in the cell by corrosion.

There is another possible mechanism for the explosion. If ignition of the hydrogen-oxygen mixture (generated by (1)) could occur in a cell, it would explode. Generally only if a dead cell is in a fairly dry state can arcing occur to ignite the hydrogen oxygen mixture. We do not know how dry this type of cell must become before arcing can occur. However, we do favor this mechanism as the initiator of the explosion. Gas generated in the cell forces part of the electrolyte into a void space in the center of the cell (see reference 1 for cell design). This space cannot hold more than about 18 cm^3 of electrolyte. For SN 210 at the time of the explosion corrosion of zinc, (2), and electrolysis of the electrolyte, (1), would have used up an additional 26 cm^3 of electrolyte. Each cell contains initially about 70 cm^3 of electrolyte. The above data indicate that at the time of the explosion there would still have been about 26 cm^3 of saturated electrolyte available for the anode and cathode areas. We do not know where it was actually distributed. Of the two batteries that exploded, SN 210 should have had the driest dead cells.

WHY TWO NOT TWENTY-FOUR EXPLOSIONS

Since the rapid generation of gases can only occur during discharge of batteries with at least one dead cell, Table 3 raises a new question. Of the 24 batteries that had one or more dead cells, one gave no discharge time and could not explode. Out of the other 23 batteries discharged with dead cells, why did only two batteries explode? When batteries were being opened, it was noted that cell stacks had often shifted in position before the potting material had solidified. In some instances there was no epoxy resin between some cells and the aluminum case of the battery. In other instances only a thin layer existed at the sides or top of the cell stack. It is plausible that as pressure built up during discharge cells vented and the epoxy resin cracked relieving the pressure in 22 batteries. In only two instances did the combination of a crimped seal on the dead cell and epoxy resin around the cell remain intact long enough for a high pressure to build up. This applies only to the first mechanism for the explosions.

A different reason for not having an explosion occur applies to both mechanisms. There is sufficient liquid mercury in dead cells to form a direct short between the negative and positive terminals of the cell. Under this condition there can be no arcing or generation of hydrogen and oxygen during discharge. The direct short acts as a wire by-passing and eliminating the anode and cathode of the dead cell from the circuit of series connected cells. In the dead cells examined, a liquid mercury bridge appeared to exist between both cylindrical anodes and the inner cylindrical cathode. We favor this as the reason more cells have not exploded. In each of two batteries one cell exploded. Either a mercury bridge had not formed in the dead cell or moving the battery had broken it.

CAUSES OF INTERNAL SHORT CIRCUITS IN CELLS

A dead cell is formed by an internal short circuit in the cell. The question this raises is why are there internal short circuits. The manufacturer of the batteries has noted that part of the multilayer separator (the cellulosic paper) deteriorates. This permits penetration of zinc into the cathode forming a short circuit. As mentioned earlier we have seen mercury in live cells. The quantity while much less than in dead cells was sufficient to form a short circuit in a cell if the globules collected together. New batteries and batteries in service are periodically given a loaded voltage test. This is a check to see if the battery is still capable of meeting its discharge requirements. The older the battery the more loaded voltage tests it will have received. On receipt at NSWC/WOL, the batteries are given an additional loaded voltage test to see if the loaded voltage is above 20.0 V. SN 254 was 19 months old when received at NSWC/WOL. It had two dead cells. Our data show that it would have had 0.2 cm^3 of liquid mercury generated in each cell by the loaded voltage test. Older batteries would have more liquid mercury formed in them by this test. Liquid mercury does move in cells. Occasionally it probably forms a short circuit between the anode and cathode in a cell.

CONCLUSIONS

From the data available we believe that two conditions are necessary before an Mk 102 Mod 0 battery can explode. The battery must have at least one dead cell, and it must be under discharge. Only if the water in a dead cell is being decomposed by electrolysis, (1), can conditions be set up to cause a battery to explode. The procedure that will prevent an explosion is to not discharge a battery with an OCV at or below 39.2V (indicating a dead cell). If for test purposes a battery with a dead cell must be discharged, it should be done with the battery in proper containment. If a battery explodes then, personnel can not be injured. This has been done with all of the Mk 102 Mod 0 batteries discharged at NSWC/WOL.

ACKNOWLEDGEMENTS

The author acknowledges the advice and discussion with D. L. Warburton on all aspects of this report. C. L. Karmel made the discharge measurements and furnished photographs of exploded batteries. M. E. DeGraba opened batteries, extracted cells, and made initial measurements on them. F. M. Bowers discussed the conditions necessary for arcing in batteries under discharge. E. E. Gubner made the atomic absorption analysis for zinc and photographed pieces of cells.

Table 1

Data for Batteries that Exploded

Serial Number	OCV V	Dead Cells	Age When Discharged Ms (months)	Time (Under Discharge) of Explosion ks (hr)	Cycles of Discharge Completed	Maximum Calculated Cell Pressure[a] MPa (kpsi)
210	37.7	2	105 (40)	421 (117)	100	104 (15.0)
705	35.3	4	110 (42)	173 (48)	41	43 (6.2)

a. Calculation based on reaction (1) and the number of cycles of discharge.

Table 2

Data for Undischarged Batteries

Serial Number	OCV V	Dead Cells	Age Ms (months)	Maximum Calculated Cell Pressure[a] MPa (kpsi)
750	39.2	1	126 (48)	61 (8.8)
751	39.2	1	126 (48)	61 (8.8)
793	37.9	2	105 (40)	51 (7.3)

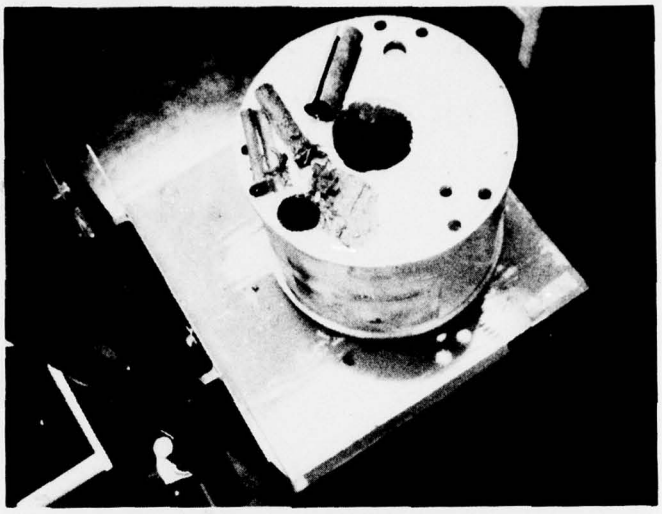
a. Calculation based on reaction (2) and the amount of zinc oxidized in the cells.

Table 3

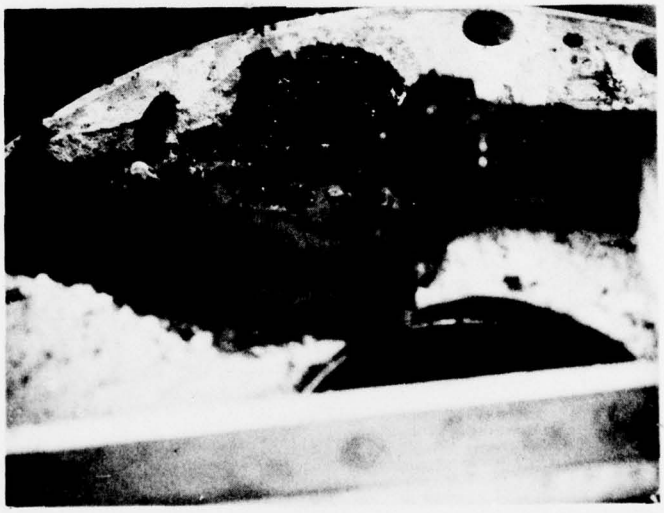
Data for Batteries with Dead Cells

Serial Number	OCV V	Dead Cells	Age When Discharged Ms (months)		Time to 20 V ks	(hr)
200	37.8	2	92	(35)	529	(147)
204	37.8	2	110	(42)	428	(119)
206	36.3	3	76	(29)	468	(130)
207	37.6	2	76	(29)	562	(156)
208	37.7	2	102	(39)	328	(91)
210	37.7	2	105	(40)	420	(116.7)[a]
211	37.6	2	92	(35)	590	(164)
214	37.7	2	84	(32)	565	(157)
215	36.7	3	74	(28)	277	(77)
221	39.4	1	92	(35)	475	(132)
224	36.4	3	89	(34)	518	(144)
254	37.7	2	50	(19)	400	(111)
259	37.8	2	82	(31)	497	(138)
705	35.3	4	110	(42)	173	(48)[a]
706	39.1	1	53	(20)	262	(73)
716	39.3	1	116	(44)	540	(150)
725	34.8	4	71	(27)	302	(84)
728	38.0	2	55	(21)	223	(62)
741	37.6	2	55	(21)	468	(130)
745	39.2	1	79	(30)	457	(127)
746	37.7	2	68	(26)	533	(148)
762	33.9	5	95	(36)	0	
773	38.9	1	92	(35)	457	(127)
798	35.0	4	74	(28)	244	(68)

a. Battery exploded at the time indicated.



a. PIECES BLOWN FROM CELL POINTING AT BLOWN HOLE



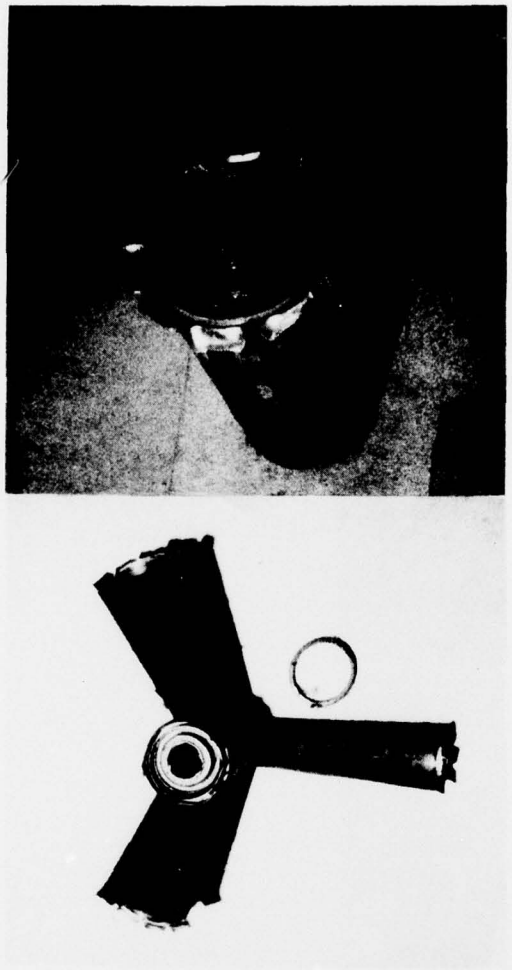
b. CLOSE-UP SHOWING MERCURY GLOBULES IN CELL

FIG. 1 BATTERY SN 705 SHOWING HOLE BLOWN IN BASE

a. LID REMOVED REVEALING BROKEN POTTING AT LEFT

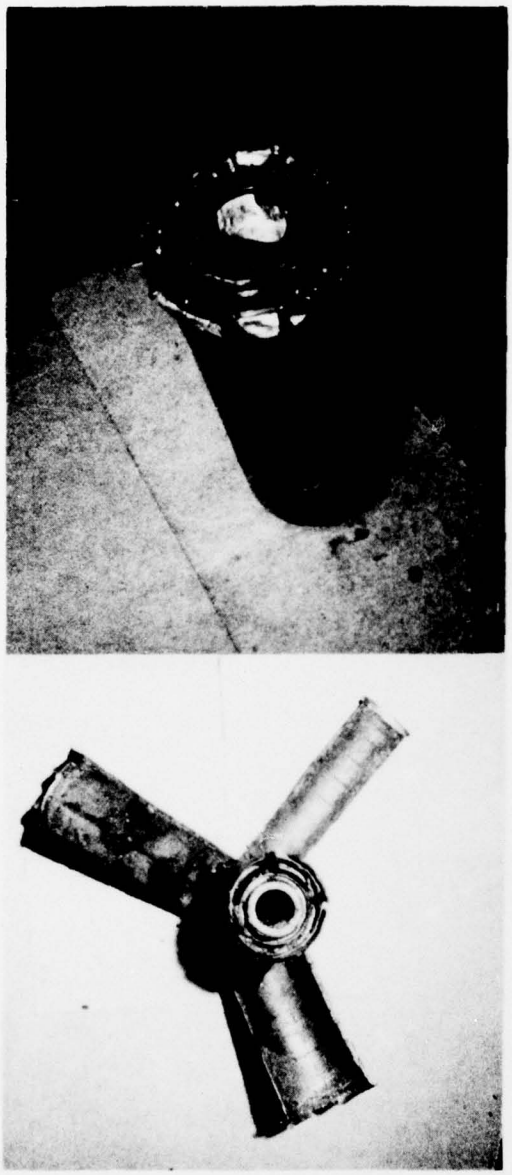
b. CLOSE UP SHOWING MERCURY GLOBULES IN CELL

FIG. 2 BATTERY SN 210 SHOWING HOLE BLOWN AT TOP



FEW GLOBULES
OF MERCURY
ARE VISIBLE

FIG. 3 UNDISCHARGED (LIVE) CELL



MANY GLOBULES
OF MERCURY
ARE VISIBLE

FIG. 4 DISCHARGED (DEAD) CELL

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